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(54) Title: CATIONIC POLYMERIZATION IN CARBON DIOXIDE

(57) Abstract

The present invention provides a method of carrying out the cationic polymerization of a monomer in carbon dioxide. The method includes the steps of (a) providing a reaction mixture comprising carbon dioxide, a monomer, a catalyst and a cationic polymerization initiator, wherein the cationic polymerization initiator is capable of initiating the cationic polymerization of the monomer, (b) polymerizing the monomer in the reaction mixture to form a polymer.

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CATIONIC POLYMERIZATION IN CARBON DIOXIDE

Related Applications

This is a continuation-in-part application of copending U.S. Application Serial No. 08/292,424, filed 18 August 1994.

5

Field of the Invention

The present invention relates to the polymerization of a monomers, and more specifically relates to the cationic polymerization of monomers in carbon dioxide.

10

Background of the Invention

Prior to about 1984, cationic polymerizations which proceed through a carbenium ion were believed to be uncontrollable due to the high reactivity of the carbenium ion. Efforts have been expended to determine counteranion, temperature and solvent conditions which will permit the living polymerization of various monomer systems. The term "cationic" polymerization as used herein refers to a positively charged (cationic) polymer chain resulting from the reaction of an initiator with a monomer.

Proper selection of initiators for cationic polymerization is essential to the generation of polymers. The proper selection of the cationic polymerization initiator in turn depends upon the monomer to be polymerized. Kennedy et al., *Polymer Bulletin* 15:317 (1986), reported the cationic polymerization of

isobutylene using an initiating system including boron trichloride with tertiary esters in chloromethane, methylene chloride, chloroethane, and mixtures of chlorinated solvents in *n*-hexane. Hagashimura et al.,
5 *Macromolecules* 22(3):1009 (1989), proposes the cationic polymerization of vinyl ethers using a weak nucleophile and a Lewis base deactivator in a solution of *n*-hexane. Nevertheless, there remains a need in the art for a method of cationically polymerizing a variety of monomers
10 while controlling the characteristics of the polymer produced.

In view of the foregoing, it is a first object of the present invention to provide a method of cationically polymerizing monomers in an environmentally
15 sound solvent, while controlling the particle size and morphology of the polymer produced.

Summary of the Invention

The present invention provides a method of carrying out the cationic polymerization of a monomer in
20 carbon dioxide. The method includes the steps of (a) providing a reaction mixture comprising carbon dioxide, a monomer, a catalyst and a cationic polymerization initiator, wherein the cationic polymerization initiator is capable of initiating the cationic polymerization of
25 the monomer; and (b) polymerizing the monomer in the reaction mixture to form a polymer.

Carbon dioxide as a polymerization solvent medium provides a number of significant advantages to polymerization systems. Traditionally, cationic
30 polymerization were conducted in a dry, inert solution dispersing medium; typically an organic solvent or a chlorinated organic solvent. Herein we describe an environmentally sound solvent alternative for cationic polymerization, namely, carbon dioxide. In addition, the
35 polymer can be easily isolated from the carbon dioxide

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solvent (i.e. the continuous phase) at the termination of polymerization, as the carbon dioxide can simply be vented from the reaction vessel. Second, the density and viscosity of carbon dioxide can be tuned over a large
5 range of conditions due to its compressibility, particularly in the supercritical phase, and thus the particle size and morphology of the polymer may be controlled.

U.S. Patent No. 5,312,882 to DeSimone et al.
10 discloses the use of supercritical carbon dioxide as a suitable solvent for heterogeneous polymerization of hydrophobic monomers. In addition, PCT Patent Application No. PCT/US93/01626 (WO93-20116) discloses the use of supercritical carbon dioxide as a suitable solvent
15 for the homogeneous polymerization of fluoromonomers as well.

The foregoing and other objects and aspects of the present invention are explained in detail in the specification set forth below.

20 Detailed Description of the Invention

Cationic polymerizations of the present invention may take place heterogeneously or homogeneously. The term "heterogeneous polymerization" as used herein refers to a polymerization carried out
25 through the use of media that create at least two separate phases (i.e., a continuous phase and a dispersed phase). In contrast, the term "homogeneous polymerization" as used herein refers to a polymerization reaction carried out through the use of media which do
30 not create more than one phase, and which are identified by being optically transparent. Heterogenous polymerizations include suspension polymerizations in which an initiator is solubilized in the dispersed phase, emulsion polymerizations in which an initiator is
35 solubilized in the continuous phase, and dispersion and precipitation polymerizations which are initially

homogeneous polymerization reactions but which nucleate particles precipitate out of solution to form a heterogeneous polymerization.

The present invention is directed to a method of carrying out the cationic polymerization of a variety of monomers in carbon dioxide. The method comprises (a) providing a reaction mixture comprising carbon dioxide, one or more monomers, a catalyst and a cationic polymerization initiator, wherein the cationic polymerization initiator is capable of initiating the cationic polymerization of the monomer(s), and (b) polymerizing the monomer(s) in the reaction mixture.

The carbon dioxide can be employed in a liquid, vapor, or supercritical phase. As used herein, "supercritical" means that a fluid medium is at a temperature that is sufficiently high that it cannot be liquified by pressure. The thermodynamic properties of carbon dioxide are reported in Hyatt, *J. Org. Chem.* 49:5097 (1984); therein, it is stated that the critical temperature of carbon dioxide is about 31°C. If liquid carbon dioxide is employed, the temperature of the reaction will be below 31°C. Preferably, the carbon dioxide is in a liquid phase. The reaction temperature should be chosen to provide sufficient heat energy to initiate and propagate the polymerization, without leading to unwanted side reactions. Preferably, the reaction temperature will be between -50°C and 200°C, and most preferably between -50°C and 31°C.

A wide variety of monomers may be employed in the method of the instant invention. The method may be employed for the polymerization of a single monomer or the copolymerization or block polymerization of two or more monomers. Monomers may be substituted or unsubstituted, saturated or unsaturated, linear or branched, cyclic or aromatic. The selection of monomer or monomers to be employed will affect the choice of

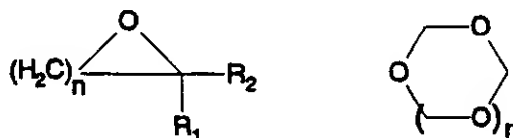
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appropriate cationic polymerization initiators, as discussed below.

Suitable monomers may be selected from a wide variety of monomers which are known to those skilled in the art as capable of undergoing cationic polymerization. Some exemplary monomers include vinyl ether monomers, cyclic ether monomers, oxazoline monomers, hydrocarbon olefin monomers, cyclic carbonate monomers, and formaldehyde. In addition, diene comonomers may be employed in copolymerization systems.

Suitable vinyl ether monomers include alkyl vinyl ethers such as methyl vinyl ether and isobutyl vinyl ether.

Suitable cyclic ether monomers include alkyl, alkoxy, and halo substituted cyclic ethers having a general formula selected from the group consisting of

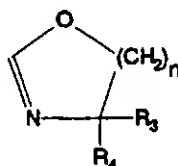


wherein R_1 and R_2 are independently selected from the group consisting of H, alkyl and preferably C_1 - C_8 alkyl, alkoxy and preferably C_1 - C_8 alkoxy, haloalkylalkoxy of the formula $(CH_2O(CH_2)_mC_xF_{2x+1})$ wherein m is 1-3 and x is 1-8, amine, amide, and alkylhaloamine of the formula $(CH_2)_zNF_2$ wherein z is 1-3, and n is a number from 1 to 5. Suitable cyclic ether monomers for use in the instant invention include 3,3-(bisethoxymethyl)oxetane, 3-(1',1'-dihydroheptafluorobutoxymethyl)-3-methyloxetane, tetrahydrofuran, trioxane, ethylene oxide. Cyclic ethers have previously been cationically polymerized in nitromethane, methylene chloride, ethylene chloride, carbon tetrachloride, and halogenated aromatic hydrocarbons. See, U.S. Patent No. 4,393,199 to Manser, and E. Goethals, *Makromol. Chem., Macromol. Symp* 42/43:51

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(1991) the disclosure of which is incorporated herein by reference in its entirety. The cyclic ether monomers can be prepared using conventional methods known to those skilled in the art, such as the methods described in U.S. Patent No. 5,210,153 to Manser et al., and H. Mark, et al., Encyclopedia of Polymer Science and Engineering, 2d ed. 10:654 (1985), the disclosures of which are incorporated herein by reference in their entirety.

Suitable oxazoline monomers include alkyl, alkoxy, and halo substituted oxazolines having a general formula

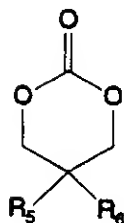


wherein R_3 and R_4 are independently selected from the group consisting of H, alkyl and preferably C_1 - C_8 alkyl, alkoxy and preferably C_1 - C_8 alkoxy, haloalkylalkoxy of the formula $(CH_2O(CH_2)_mC_xF_{2x+1})$ wherein m is 1-3 and x is 1-8, amine, amide, and alkylhaloamine of the formula $(CH_2)_zNF_2$ wherein z is 1-3, and n is a number from 1 to 5. Exemplary cyclic ether monomers for use in the instant invention include 2-ethyl oxazoline, 2-methyl oxazoline, 2-(1,1,2,2-tetrahydroperfluorooctane) oxazoline.

Suitable hydrocarbon olefin monomers include substituted or unsubstituted styrene, such as *p*-methoxy styrene and alkylene monomers such as isobutylene and propene.

Suitable cyclic carbonate monomers include compounds having the formula

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wherein R₅ and R₆ are independently selected from the group consisting of H, alkyl and preferably C₁-C₈ alkyl, alkoxy and preferably C₁-C₈ alkoxy, and haloalkylalkoxy of the formula (CH₂O(CH₂)_mC_xF_{2x+1}) wherein m is 1-3 and x is 1-8.

Suitable diene comonomers include butadiene, and isoprene.

The cationic polymerization is typically catalyzed by the addition of one or more cationic polymerization catalysts. The catalysts may be provided independently of the other reactants, or may be premixed or coupled with the initiator. Suitable catalysts will depend upon the particular polymerization system (i.e., monomer(s) and initiator) to be polymerization.

Suitable cationic polymerization catalysts for the polymerization of vinyl ether monomers include ethyl aluminum dichloride. According to one preferred embodiment, the ethyl aluminum dichloride catalyst and the initiator are provided in the reaction in the form of a catalyst/initiator couple. Preferably, the catalyst and initiator are premixed and coupled prior to reaction with the vinyl ether monomer.

Suitable cationic polymerization catalysts for the polymerization of cyclic ethers and oxazolines include boron trifluoride tetrahydrofuranoate.

Suitable cationic polymerization catalysts for the polymerization of hydrocarbon olefins include tin tetrachloride, titanium tetrachloride, boron trichloride, boron trifluoride.

Suitable cationic polymerization catalysts for the polymerization of cyclic carbonates and formaldehyde include boron trifluoride.

The polymerization is initiated by the addition
5 of a cationic polymerization initiator. The selection of a suitable cationic polymerization initiator will necessarily depend upon the monomer or monomers to be polymerized, and their compatibility with carbon dioxide. The polymerization of vinyl ether monomers is typically
10 initiated by the addition of a cationic polymerization initiator comprising an ester initiator and a Lewis base deactivator. The ester initiator comprises an adduct of acetic acid and isobutyl vinyl ether. Suitable Lewis base deactivators include ethyl acetate.

15 The polymerization of cyclic ether monomers is typically initiated by the addition of a cationic polymerization initiator comprising a strong acid, a Lewis acid, or a preinitiator. Exemplary strong acids for use in as cationic polymerization initiators of
20 cyclic ethers include triflic acid. Suitable Lewis acid initiators include boron trifluoride. Suitable preinitiators include water, alcohols, ethers and esters. One preferred preinitiator is butanediol.

The polymerization of oxazoline monomers is
25 typically initiated by the addition of a cationic polymerization initiator comprising a strong acid, a Lewis acid, or a preinitiator. Exemplary strong acids and Lewis acids are described above. In addition, preinitiators such as those described above may be
30 included.

The polymerization of hydrocarbon olefin monomers is typically initiated by the addition of a cationic polymerization initiator selected from the group consisting of 1-chloro-1-phenyl ethane, 2-chloro-2,4,4-
35 trimethylpentane, tertiary ethers, Lewis bases, or 2-methoxy-2-propyl benzene. Suitable Lewis bases include dimethyl sulfoxide, acetamide, or ethyl acetate. The

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initiator may also comprise a deactivator, such as tetrabutylammonium chloride or the like. Accordingly to one preferred embodiment, styrene is cationically polymerized using 1-chloro-1-phenyl ethane and
5 tetrabutylammonium chloride as the initiator. According to a second preferred embodiment, isobutylene is cationically polymerized using 2-chloro-2,4,4-trimethylpentane as the initiator.

The polymerization of cyclic carbonate monomers
10 is typically initiated by the addition of a cationic polymerization initiator comprising methyl triflate, methyl iodide, or benzyl bromide. The use of these initiators in the cationic polymerization of cyclic carbonate monomers in methylene chloride was previously
15 reported in T. Endo, et al., *J. of Poly. Sci.:Part A:Poly. Chem.*, 31:581 (1993) the disclosure of which is incorporated herein by reference in its entirety.

The polymerization of formaldehyde is typically initiated by the addition of a cationic polymerization
20 initiator comprising strong acids or Lewis acids and a preinitiator. One suitable strong acid is hydrochloric acid. A suitable Lewis acid is boron trifluoride. A suitable preinitiator is water. The use of this initiator system was previously reported in M. Stevens
25 Polymer Chemistry, 2nd ed., Oxford University Press, 355-366 (1990), the disclosure of which is incorporated herein by reference in its entirety for the polymerization of formaldehyde in hydrocarbon solvents.

The reaction mixture may be homogeneous or
30 heterogeneous depending upon the monomer or monomers to be polymerized. In some cases, the polymerization is a dispersion polymerization meaning that the reaction mixture may initially be homogeneous and becomes heterogeneous as the polymer nucleates a particle which
35 is not soluble in the solvent.

The polymerization reaction mixture may include other additives and reactants known to those skilled in

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the art. For example in one preferred embodiment, the process of the invention includes the addition of surfactant for stabilizing the monomer and polymer in the polymerization medium. The surfactant should be one that is surface active in carbon dioxide and thus partitions itself at the carbon dioxide-monomer interface. Suitable surfactants are described in detail in U.S. Patent No. 5,312,882 to DeSimone et al., the disclosure of which is incorporated herein by reference in its entirety. Such a surfactant should lower the interfacial tension between the carbon dioxide polymerization medium and the polymer, and thus create a dispersed phase. The surfactant is generally present in the reaction mixture in a concentration of from about 0.001 up to about 30 percent by weight. The surfactants can be nonreactive in the polymerization or can react with and thereby be included with the forming polymer. See, e.g., U.S. Pat. Nos. 4,592,933 and 4,429,666 for exemplary reactive surfactants.

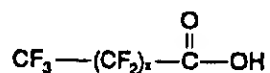
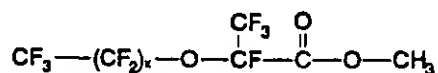
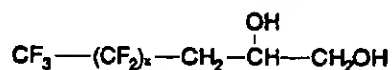
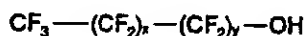
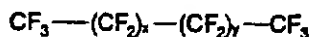
The surfactant should contain a segment that is soluble or interfacially active in carbon dioxide ("CO₂-philic"). Exemplary CO₂-philic segments include a fluorine-containing segment, such as can be found in fluoropolymers or copolymers of fluoropolymers, or a siloxane-containing segment, such as can be found in siloxane polymers or copolymers of siloxane polymers. As used herein, a "fluoropolymer" has its conventional meaning in the art. Exemplary fluoropolymers are those formed from: fluoroacrylate monomers such as 2-(N-ethylperfluorooctanesulfonamido) ethyl acrylate ("Et-FOSEA"), 2-(N-ethylperfluorooctanesulfonamido) ethyl methacrylate ("EtFOSEMA"), 2-(N-methylperfluorooctanesulfonamido) ethyl acrylate ("MeFOSEA"), 2-(N-methylperfluorooctanesulfonamido) ethyl methacrylate ("MeFOSEMA"), 1,1-Dihydroperfluorooctyl acrylate ("FOA"), 1,1-dihydroheptafluorobutoxy methyl oxetane (p(FOX7)), and 1,1-Dihydroperfluorooctyl acrylate

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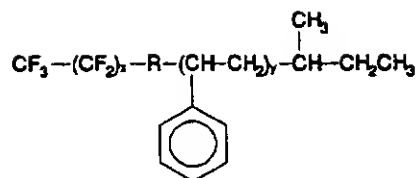
("FOMA"); fluoroolefin monomers such as tetrafluoroethylene, fluorostyrene monomers such as α -fluorostyrene, β -fluorostyrene, α , β -difluorostyrenes, β , β -difluorostyrenes, α , β , β -trifluorostyrenes, α -trifluoromethylstyrenes, 2,4,6-Tris(trifluoromethyl)styrene, 2,3,4,5,6-pentafluorostyrene, 2,3,4,5,6-pentafluoro- α -methylstyrene, and 2,3,4,5,6-pentafluoro- β -methylstyrene; fluoroalkylene oxide monomers such as perfluoropropylene oxide and perfluorocyclohexene oxide; fluorinated vinyl alkyl ether monomers; and the copolymers thereof with suitable comonomers, wherein the comonomers are fluorinated or unfluorinated. Exemplary siloxane-containing compounds include alkyl, fluoroalkyl, and chloroalkyl siloxanes.

More preferably, the surfactant comprises a "CO₂-phobic" group along with a CO₂-soluble group, such as a fluoropolymer. The CO₂-phobic group may be a hydrophobic group, such as a polystyrene group, or a hydrophilic group such as carboxylic acid. Such copolymers can take many forms; exemplary forms are graft copolymers, random copolymers, and block copolymers.

Other suitable surfactants that are surface active in carbon dioxide include

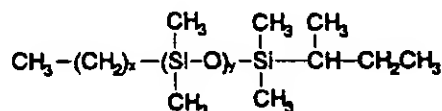
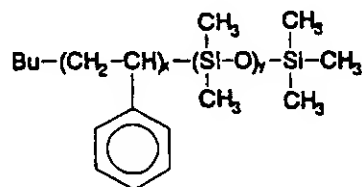


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where $x=1-30$ and $y=1$ to 30 . The x and y values are chosen to adjust the balance between "CO₂-philic" and "CO₂-phobic" to tailor the surface activity of the reagents.

- 5 Exemplary silicone-containing surfactants (i.e., siloxane polymers or copolymers) include



wherein x and y are varied to adjust to "CO₂-philic" and "CO₂-phobic" balance.

- The polymerizing step of the present invention
- 10 can be carried out by polymerization methods using apparatus and conditions known to those skilled in this art. For example, the polymerization reaction is carried out in a suitable high pressure reaction vessel of about 24 mL and capable of withstanding pressures on the order
- 15 of up to about 8000 psi. The reaction vessel typically includes a cooling system. Additional features of the reaction vessel used in accordance with the invention include heating means such as an electric heating furnace to heat the reaction mixture and mixing means, i.e.,
- 20 stirrers such as paddle stirrers, impeller stirrers, or multistage impulse countercurrent agitators, blades, and

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the like. Typically, the reaction begins by cooling the reaction vessel to a temperature below about 31°C. The initiator, monomer or monomers, and carbon dioxide are added to the vessel. Typically the mixture is allowed to
5 polymerize for between about 2 and 24 hours, and preferably is stirred as the reaction proceeds. At the conclusion of the reaction, the polymer can be collected by methods such as venting of the carbon dioxide or by fractionation. After separation, the polymer can be
10 collected by conventional means. In addition, the polymers of the present invention may be retained in the carbon dioxide, and sprayed onto a surface. After the carbon dioxide and solvent evaporate, the polymer forms a coating on the surface.

15 The polymer formed by the present invention can also be used to form molded articles, such as valves and bottles, films, fibers, resins, and matrices for composite materials.

The present invention is explained in greater
20 detail in the following examples. As used herein, "M" means molar concentration, "NMR" means nuclear magnetic resonance, "MHz" means megahertz, "GPC" means gas phase chromatography, "Å" means angstroms, "UV" means ultraviolet, "g" means grams, "mol" means moles, "mL"
25 means milliliters, "C" means degrees Centigrade, "S" means seconds, "h" means hours, "psig" means pounds per square inch (gauge), "M_n" means number average molecular weight, "MWD" means molecular weight distribution, "f" means functionality, "ppm" means parts per million, "T_g"
30 means glass transition temperature, "nm" means nanometers, "mg" means milligrams, "rpm" means revolutions per minute, "mm Hg" means millimeters of mercury, and "psi" means pounds per square inch. These Examples are illustrative and are not to be taken as
35 limiting of the invention.

EXAMPLE 1

Experimental Procedures and Materials

Monomers of isobutyl vinyl ether, styrene, and 3,3'-bisethoxymethyl oxetane were provided by Dr. Gerald Manser of Aerojet Corporation. Bisethoxymethyl oxetane (BEMO) was vacuum distilled at 5×10^{-2} mm Hg, with the fraction distilling at 54°C to 57°C being collected. Styrene was vacuum distilled from calcium hydride at 5×10^{-2} mm Hg and 50°C. Isobutyl vinyl ether was distilled twice from calcium hydride under an argon atmosphere at about atmospheric pressure and a temperature of 82°C. Lewis acid catalysts ethyl aluminum dichloride (1.0 M in hexanes, obtained from Aldrich) and tin tetrachloride (obtained from Aldrich) were used without further purification. Lewis acid catalyst boron trifluoride tetrahydrofuranoate ($\text{BF}_3\text{-THF}$) was prepared by stirring boron trifluoride diethyletherate (obtained from Aldrich) with prechilled tetrahydrofuran (obtained from Mallinckrodt) for two hours at 25°C. $\text{BFC}_3\text{-THF}$ was purified by distillation at 100° under argon to remove volatiles, followed by vacuum distillation with the fraction distilling at 70°C being isolated. The acetic acid/isobutyl vinyl ether adduct was prepared as described by T. Hagashimura et al. *Macromolecules* 22(3): 1009 (1989). Isobutyl vinyl ether (IBVE) was treated with acetic acid for three hours at 60°C and atmospheric pressure, then the adduct was distilled twice under vacuum at 5×10^{-2} mm Hg with the middle fraction, which is distilled over at about 60°C, being collected both times to prepare the ester initiator.

Initiators 1,4-butanediol, 2,2,2-trifluoroethanol, and 1-phenyl-1-chloroethane (obtained from Aldrich) were used without further purification. The deactivator, ethyl acetate was obtained from Aldrich and was distilled twice from calcium hydride under an argon atmosphere. Cyclohexane was obtained from Phillips Petroleum and was stirred over concentrated sulfuric acid

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for two weeks, decanted, and distilled from sodium metal under an argon atmosphere. Methylene chloride was obtained from Mallinckrodt, and, was distilled twice from calcium hydride under an argon atmosphere. Carbon
5 dioxide was obtained from Matheson, 99.99% was passed through copper oxide catalyst column to remove trace amounts of oxygen and then through a 3Å molecular sieve column to remove trace amounts of moisture. The high pressure reactor was constructed from Hastelloy C-22,
10 having a volume of 24 mL and a pressure capacity of up to about 8000 psi and was obtained from Haynes International.

EXAMPLE 2

Polymerization in Cyclohexane in the Absence of Ester Initiator

15 Before running polymerization in supercritical carbon dioxide, a series of polymerization were conducted in cyclohexane. The monomer employed was isobutyl vinyl ether.

A 300 mL round-bottom glass flask equipped with
20 a teflon stirring bar and sealed with a rubber septa, is flame dried under an argon atmosphere. IBVE (10 mL, 7.68 g), ethyl acetate (10 mL), and cyclohexane (30 mL) were combined in the flask. The temperature of the flask is maintained near 40°C using a water bath, and stirring is
25 achieved using a stir plate. Ethyl aluminum dichloride (EtAlCl₂) (0.38 mL, 0.38 mmol) is added via syringe to catalyze the polymerization, with trace amounts of water being added as the initiator. The reaction proceeds for twelve hours at which time a solution of sodium ethoxide
30 in ethanol is added to the flask to terminate the reaction. The resulting polymer is precipitated into methanol, filtered, and dried in vacuum overnight. The polymerization conditions, yields and molecular weight data are summarized in Table 1.

TABLE 1

Sample	feed ratio				Mw ($\times 10^{-3}$)	Mn ($\times 10^{-3}$)	MWD	Yield
	monomer (g)	ethyl acetate (mL)	EtAlCl ₂ (mmol)	solvent (mL)				
mrcA137	3.072	4	0.31	12	165	107	1.5	--
mrcB137	7.68	10	0.38	30	134	80	1.7	--

5 both polymerizations are run at 40°C

EXAMPLE 3

Polymerization of Isobutyl vinyl ether (IBVE) in Supercritical

Carbon Dioxide in the Absence of Ester Initiator

Ethyl acetate (3 mL) and EtAlCl₂ (0.46 mL, 0.46
 10 mmol) are added to the high pressure cell via syringe
 under an argon atmosphere. The cell is equipped with a
 teflon coated stir bar and heated to 40°C. Carbon
 dioxide is added to the cell using a high pressure
 syringe to achieve a cell pressure of 4500 psi. IBVE (3
 15 mL, 2.304 g) is added to the cell using a high pressure
 syringe. The reaction continued for fourteen (14) hours
 and was accompanied by a pressure drop, to a final
 pressure of 3683 psi. During the course of the reaction,
 polymer could be seen forming and precipitating from the
 20 carbon dioxide fluid.

At the end of the polymerization, carbon
 dioxide is vented slowly to leave the polymer in the
 cell. The reaction is terminated using a solution of
 sodium ethoxide in ethanol. The polymer is then
 25 dissolved in cyclohexane or a solution of
 cyclohexane/tetrahydrofuran, precipitated into a large
 excess of methanol, filtered and dried in vacuum
 overnight. Poly(isobutyl vinyl ether) (1.997 g) was
 recovered. (Yield = 87%).

30 Characterizations: ¹H NMR spectra show the
 expected patterns, without vinyl proton peaks of the
 monomer and without any indication of incorporation of
 carbon dioxide into the polymer backbone. The FTIR

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spectrum are consistent with the corresponding homopolymer made in cyclohexane, with no carbonyl peak present. Gel permeation chromatography (GPC) analysis show $M_n = 1.51 \times 10^5$, $M_w = 5.99 \times 10^5$, and $MWD = 4.0$.

5

EXAMPLE 4

Polymerization of Isobutyl vinyl ether (IBVE) in Supercritical

Carbon Dioxide in the Absence of Ester Initiator

Ethyl acetate (4 mL) and ethyl aluminum dichloride (0.25 mL, 0.25 mmol) are added to the high pressure cell. Following the same procedure in **Example 3**, carbon dioxide and isobutyl vinyl ether (4 mL, 3.702 g) are added for a final pressure of 4200 psi. The reaction proceeds for twenty-two hours at 40°C, during which time pressure within the cell decreases to 3860 psi. Poly(IBVE) (2.211 g) is recovered. (Yield = 72%).

Characterization: ^1H NMR and FTIR spectra are consistent with those of the homopolymer made in cyclohexane. GPC indicates $M_n = 8.0 \times 10^4$, $M_w = 5.2 \times 10^5$, and $MWD = 6.5$.

20

EXAMPLE 5

Polymerization of Isobutyl vinyl ether (IBVE) in Supercritical

Carbon Dioxide in the Absence of Ester Initiator

Ethyl acetate (4 mL) and ethyl aluminum dichloride (0.5 mL, 0.5 mmol) are added to the high pressure cell. Following the same procedure as described in **Example 3**, carbon dioxide and IBVE (4 mL, 3.072 g) are added for a final pressure of 4200 psi. The reaction proceeds for 23 hours at 40°C. Poly(IBVE) (1.277 g) is recovered. (Yield = 44%).

30

Characterizations: ^1H NMR and FTIR spectra are consistent with those of the homopolymer made in cyclohexane. GPC indicates $M_n = 5.2 \times 10^4$, $M_w = 2.8 \times 10^5$, and $MWD = 5.4$.

EXAMPLE 6

Comparative Example: Polymerization in Cyclohexane in the Presence of Ester Initiator

A 300 mL round-bottom glass flask equipped with
5 a teflon stirring bar and sealed with a rubber septa, is
flame dried under an argon atmosphere. IBVE (10 mL, 7.68
g), ethyl acetate (9.8 mL), the ester initiator (0.06 mL,
0.31 mmol), and cyclohexane (100 mL) are combined in the
flask. The temperature of the flask is maintained near
10 40°C using a water bath and stirring is achieved with a
stir plate. Ethyl aluminum dichloride (EtAlCl_2) (0.40 mL,
0.40 mmol) is added via syringe to catalyze the
polymerization. The reaction proceeds for twenty-four
hours at which time a solution of sodium ethoxide in
15 ethanol is added to the flask to terminate the reaction.
The resulting polymer is precipitated into methanol,
filtered, and dried in vacuum overnight. Poly(IBVE)
(3.35 g) is recovered. (Yield = 44%).

Characterization: GPC indicates $M_n = 7.0 \times 10^3$,
20 $M_w = 8.1 \times 10^3$, MWD = 1.15.

EXAMPLE 7

Polymerization of Isobutyl vinyl ether (IBVE) in Supercritical Carbon Dioxide in the Presence of Ester Initiator

Ethyl acetate (2.4 mL), EtAlCl_2 (0.2 mL, 0.2
25 mmol), and the ester initiator (0.04 mL, 0.23 mmol) are
combined in the cell. Following the procedure as
described in **Example 3**, carbon dioxide and IBVE (3 mL,
2.304) are added to achieve a pressure of 4800 psi. The
reaction proceeds for thirteen hours at 40°C, during
30 which time the pressure within the cell drops to 3800
psi. Poly(IBVE) (2.11 g) is recovered. (Yield = 91%).

Characterization: ^1H NMR and FTIR spectra are
consistent with those of the homopolymer made in
cyclohexane. GPC indicates $M_n = 6.7 \times 10^3$, $M_w = 1.2 \times$
35 10^4 , and MWD = 1.8.

EXAMPLE 8

Polymerization of Isobutyl vinyl ether (IBVE) in SupercriticalCarbon Dioxide in the Presence of Ester Initiator

Ethyl acetate (2.4 mL), EtAlCl_2 (0.2 mL, 0.2 mmol), and the ester initiator (0.01 mL, 0.06 mmol) are combined in the cell. Following the same procedure as described in **Example 3**, carbon dioxide and IBVE (3 mL, 2.304) are added to achieve a pressure of 5000 psi. The reaction proceeds for twelve hours, during which time the pressure drops to 4041 psi.

Characterization: ^1H NMR and FTIR spectra are consistent with those of the homopolymer made in cyclohexane.

EXAMPLE 9

Polymerization of Isobutyl vinyl ether (IBVE) in LiquidCarbon Dioxide in the Presence of Ester Initiator

Ethyl acetate (2.4 mL), EtAlCl_2 (0.2 mL, 0.2 mmol), and the ester initiator (0.04 mL, 0.23 mmol) are combined in the cell. Following the same procedure described in **Example 3**, carbon dioxide and IBVE (3 mL, 2.304 g) are added to a pressure of 5200 psi. The reaction proceeds for twelve hours at 30°C , during which time the pressure drops to 3236 psi.

Characterization: ^1H NMR and FTIR spectra are consistent with those of the homopolymer made in cyclohexane. GPC indicates $M_n = 1.4 \times 10^4$, $M_w = 2.0 \times 10^4$, MWD = 1.4.

EXAMPLE 10

Polymerization of Isobutyl vinyl ether (IBVE) in SupercriticalCarbon Dioxide in the Presence of Ester Initiator

Ethyl acetate (2.4 mL), EtAlCl_2 (0.2 mL, 0.2 mmol), and the ester initiator (0.04 mL, 0.23 mmol) are combined in the cell. Following the same procedure

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described in **Example 3**, carbon dioxide and IBVE (3 mL, 2.304 g) are added to a pressure of 5000 psi. The reaction proceeds for twelve hours at 60°C, during which time the pressure drops to 4200 psi. Poly(IBVE) (2.043 g) is recovered. (Yield = 92%).

Characterization: ^1H NMR and FTIR spectra are consistent with those of the homopolymer made in cyclohexane. GPC indicates $M_n = 1.4 \times 10^4$, $M_w = 2.0 \times 10^4$, MWD = 1.4.

10

EXAMPLE 11

Polymerization of Isobutyl vinyl ether (IBVE) in Supercritical

Carbon Dioxide in the Presence of Ester Initiator

Ethyl acetate (1.2 mL), EtAlCl_2 (0.2 mL, 0.2 mmol), and the ester initiator (0.04 mL, 0.23 mmol) are combined in the cell. Following the same procedure described in **Example 3**, carbon dioxide and IBVE (3 mL, 2.304 g) are added. The reaction proceeds for twelve hours at 40°C. Poly(IBVE) (1.994 g) is recovered. (Yield = 87%).

20

Characterization: ^1H NMR and FTIR spectra are consistent with those of the homopolymer made in cyclohexane. GPC indicates $M_n = 2.3 \times 10^4$, $M_w = 8.7 \times 10^4$, MWD = 3.9.

EXAMPLE 12

25

Polymerization of Isobutyl vinyl ether (IBVE) in Supercritical

Carbon Dioxide in the Presence of Ester Initiator

Ethyl acetate (4.8 mL), EtAlCl_2 (0.2 mL, 0.2 mmol), and the ester initiator (0.04 mL, 0.23 mmol) are combined in the cell. Following the same procedure described in **Example 3**, carbon dioxide and IBVE (3 mL, 2.304 g) are added to the cell to a pressure of 5000 psi. The reaction proceeds for twelve hours at 40°C, during which time the pressure drops to 4050 psi. Poly(IBVE) (1.063 g) is recovered. (Yield = 46%).

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Characterization: ^1H NMR and FTIR spectra are consistent with those of the homopolymer made in cyclohexane. GPC indicates $M_n = 3.4 \times 10^3$, $M_w = 4.8 \times 10^3$, $MWD = 1.4$.

5

EXAMPLE 13

Polymerization of Isobutyl vinyl ether (IBVE) in Supercritical Carbon Dioxide in the Presence of Ester Initiator

EtAlCl₂ (0.2 mL, 0.2 mmol), and the ester initiator (0.04 mL, 0.23 mmol) are combined in the cell. Following the same procedure described in Example 3, carbon dioxide and IBVE (3 mL, 2.304 g) are added to the cell to a pressure of 5000 psi. The reaction proceeds for twelve hours at 40°C, during which time the pressure drops to 3300 psi. Poly(IBVE) (1.614 g) is recovered. (Yield = 70%).

Characterization: ^1H NMR and FTIR spectra are consistent with those of the homopolymer made in cyclohexane. GPC indicates $M_n = 1.3 \times 10^4$, $M_w = 3.9 \times 10^4$, $MWD = 2.9$.

20

EXAMPLE 14

Polymerization of Isobutyl vinyl ether (IBVE) in Supercritical Carbon Dioxide in the Presence of Ester Initiator

Ethyl acetate (2.4 mL), EtAlCl₂ (0.2 mL, 0.2 mmol), and the ester initiator (0.02 mL, 0.12 mmol) are combined in the cell. Following the same procedure described in Example 3, carbon dioxide and IBVE (3 mL, 2.304 g) are added to the cell to a pressure of 4500 psi. The reaction proceeds for twelve hours at 40°C. Poly(IBVE) (2.245 g) is recovered. (Yield = 93%).

30

Characterization: ^1H NMR and FTIR spectra are consistent with those of the homopolymer made in cyclohexane. GPC indicates $M_n = 1.4 \times 10^4$, $M_w = 2.0 \times 10^4$, $MWD = 1.4$.

EXAMPLE 15

Polymerization of Isobutyl vinyl ether (IBVE) in SupercriticalCarbon Dioxide in the Presence of Ester Initiator

Ethyl acetate (2.0 mL), EtAlCl_2 (0.2 mL, 0.2 mmol), and the ester initiator (0.02 mL, 0.12 mmol) are combined in the cell. Following the same procedure described in **Example 3**, carbon dioxide and IBVE (3 mL, 2.304 g) are added to the cell to a pressure of 4955 psi. The reaction proceeds for twelve hours at 60°C, during which time the pressure had dropped to 3957 psi.

Characterization: ^1H NMR and FTIR spectra are consistent with those of the homopolymer made in cyclohexane. GPC indicates a bimodal molecular weight distribution.

EXAMPLE 16

Comparative Example: Polymerization of 3,3'-bisethoxymethyl oxetane in Methylene Chloride

Polymers of 3,3'-(bisethoxymethyl)oxetane (BEMO) are prepared in methylene chloride. A 300 mL round-bottom glass flask equipped with a teflon stirring bar and sealed with a rubber septa, was flame dried under an argon atmosphere. BEMO (4 mL, 3.99 g), and methylene chloride (20 mL) are combined in the flask. If no external proton source (i.e., initiator) is added, adventitious water was employed as the proton source. The temperature of the flask is maintained near 10°C using an ice bath and stirring is achieved with a stir plate. The catalyst boron trifluoride tetrahydrofuranoate ($\text{BF}_3\text{-THF}$) (0.06 mL, 0.58 mmol) is added via syringe to catalyze the polymerization, with trace amounts of water being added as the initiator. The reaction proceeds for four hours at which time a solution of aqueous sodium hydroxide is added to the flask to terminate the reaction. The resulting polymer is precipitated into methanol, filtered, and dried in vacuum

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overnight. Table 2 summarizes the results obtained in methylene chloride.

Table 2

	Sample	feed ratio				Mw	Mn	MWD	Yield
		monomer (g)	proton source	BF ₃ -THF (mmol)	solvent (mL)	($\times 10^{-3}$)	($\times 10^{-3}$)		
5	mc11094B	3.99	--	0.58	20	19.9	35.9	1.8	67%
	mc11194	3.99	--	0.58	20	17.6	34.9	1.9	70%
	mcBF3A	3.99	--	0.58	20	29.3	63.7	2.2	77%
	mcBDOA	3.99	BDO	1.16	20	17.9	30.5	1.7	37%
	mc5494	3.99	CF3CH2OH	0.58	20	33.2	72.4	2.2	79%
10	mc51094	3.99	CF3CH2OH	2.32	20	28.0	55.6	1.7	64%
	mc51894	3.99	CF3CH2OH	2.32	20	28.1	57.1	2.0	76%

EXAMPLE 17

Polymerization of 3,3'-(bisethoxymethyl)oxetane (BEMO)

in Liquid Carbon Dioxide

- 15 The high pressure cell is equipped with a Hastelloy C-22 dish to allow both monomer and catalysts to be added to the cell before the carbon dioxide and not premix. BEMO (4.8 mL, 4.8 g) is added to the body of the high pressure cell via syringe under an argon atmosphere.
- 20 BF₃-THF (0.28 mL, 0.69 mmol) is added to the Hastelloy dish via syringe under an argon atmosphere. The cell is equipped with a stir bar and the temperature is maintained near -10°C using a sodium chloride/ice bath. Carbon dioxide is added to the cell using an ISCO™ high
- 25 pressure syringe pump to a pressure of 4300 psi. The reaction proceeds for four hours, during which time the pressure drops to 3500 psi. Carbon dioxide is slowly vented and the reaction is terminated using an aqueous solution of sodium hydroxide. The polymer is dissolved
- 30 in tetrahydrofuran and precipitated in methanol, filtered, washed with dilute hydrochloric acid and water,

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then dried overnight in a vacuum. Poly(BEMO) (3.210 g) is recovered. (Yield = 67%)

Characterization: ^1H NMR and FTIR spectra are consistent with those of the homopolymer prepared in methylene chloride. GPC indicates $M_n = 8.1 \times 10^3$, $M_w = 2.2 \times 10^4$, MWD = 2.7.

EXAMPLE 18

Polymerization of 3,3'-(bisethoxymethyl)oxetane (BEMO)

in Liquid Carbon Dioxide

10 Reaction is conducted as described in **Example 17**. Carbon dioxide is added to a pressure of 4800 psi. Poly(BEMO) (1.484 g) is recovered. (Yield = 31%).

Characterization: ^1H NMR and FTIR spectra are consistent with those of the homopolymer made in methylene chloride. GPC indicates $M_n = 9.0 \times 10^3$, $M_w = 2.8 \times 10^4$, MWD = 3.1.

EXAMPLE 19

Polymerization of 3,3'-(bisethoxymethyl)oxetane (BEMO)

in Liquid Carbon Dioxide

20 BEMO (4.8 mL, 4.8 g) and 1,4-butanediol (0.06 mL, 0.69 mmol) are added to the cell. Following the same procedure described in **Example 17**, BF_3 -THF (0.15 mL, 1.38 mmol) is added to the cell. Carbon dioxide is added to an initial pressure of 4800 psi. Poly(BEMO) (2.08 g) is
25 recovered. (Yield = 43%).

Characterization: ^1H NMR and FTIR spectra are consistent with those of the homopolymer made in methylene chloride. GPC indicates $M_n = 7.3 \times 10^3$, $M_w = 1.2 \times 10^4$, MWD = 1.6.

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EXAMPLE 20

Polymerization of 3,3'-(bisethoxymethyl)oxetane (BEMO) in Liquid Carbon Dioxide

Reaction is conducted as described in **Example**
5 18, except the initial pressure of carbon dioxide is 3000
psi. Poly(BEMO) (0.74 g) is recovered. (Yield = 16%).

Characterization: ¹H NMR and FTIR spectra are
consistent with those of the homopolymer made in
methylene chloride. GPC indicates $M_n = 1.0 \times 10^4$, $M_w =$
10 1.6×10^4 , MWD = 1.6.

EXAMPLE 21

Polymerization of 3,3'-(bisethoxymethyl)oxetane (BEMO) in Liquid Carbon Dioxide

Reaction is conducted as described in **Example**
15 19, except that 1,4-butanediol is premixed with BF³-THF
and then injected into the reactor dish. BEMO (4.8 mL,
4.8 g) is added to the body of the cell. BDO/BF³-THF
solution (0.22 mL, 0.69 mmol) is injected into the dish
within the cell. Carbon dioxide is added to a pressure
20 of 4200 psi. Poly(BEMO) (0.840 g) is recovered.
(Yield = 18%).

Characterization: ¹H NMR and FTIR spectra are
consistent with those of the homopolymer made in
methylene chloride. GPC indicates $M_n = 1.2 \times 10^4$, $M_w =$
25 2.0×10^4 , MWD = 1.7.

EXAMPLE 22

Comparative Example: Polymerization of Styrene in Methylene Chloride

Polymers of styrene are prepared in methylene
30 chloride using a method outlined by T. Higashimura et
al., *Macromolecules* 26:744 (1993).

A 300 mL round-bottom glass flask equipped with
a teflon stirring bar and sealed with a rubber septa, is
flame dried under an argon atmosphere. Styrene (4.0 mL,

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3.64 g), the initiator, 1-chloro-1-phenyl ethane (0.5 mL, 0.70 mmol), the deactivator, tetrabutyl ammonium chloride (2.4 mL, 1.40 mmol), and methylene chloride (20 mL) are added to the flask via syringe. The temperature of the flask is maintained near -10°C using an ice bath and stirring is achieved with a stir plate. The catalyst, tin tetrachloride (0.7 mL, 3.49 mmol) is added to the cell via syringe. The reaction proceeds for 3 hours at -10°C, at which time the reaction is terminated by the addition of a solution of sodium methoxide and methanol. The polymer is precipitated into methanol, filtered, and dried overnight under vacuum. Poly(styrene) (2.813 g) is recovered. (Yield = 77%).

Characterization: GPC indicates $M_n = 4.2 \times 10^3$, $M_w = 4.9 \times 10^3$, MWD = 1.17.

EXAMPLE 23

Polymerization of Styrene in Liquid Carbon Dioxide

The high pressure cell is equipped with a Hastelloy C-22 dish to allow both monomer and catalysts to be added to the cell before the carbon dioxide without premixing. Styrene (5.0 mL, 4.55 g), 1-chloro-1-phenyl ethane (0.1 mL, 0.87 mmol), and tetrabutylammonium chloride (1.9 mL, 1.7 mmol) are added to the body of the high pressure cell via syringe under an argon atmosphere. Tin tetrachloride (0.9 mL, 4.41 mmol) is added to the Hastelloy dish via syringe under an argon atmosphere. The cell is equipped with a stir bar and temperature is maintained near 0°C using a NESLAB™ circulating bath equipped with a refrigeration unit and a solution of water and ethylene glycol as the coolant. Carbon dioxide is added to the cell using an ISCO™ high pressure syringe pump to a pressure of 4500 psi. Within minutes, polymer can be seen forming and precipitating out of solution in the reactor. The polymerization proceeds for 3 hours near 0°C, during which time the pressure drops to approximately 4000 psi. The carbon dioxide is then

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slowly vented off and the reaction is terminated by the addition of a solution of sodium methoxide and methanol. The polymer is dissolved in tetrahydrofuran, precipitated into methanol, filtered, and dried under vacuum
5 overnight. Poly(styrene) (2.3838 g) is recovered. (Yield = 52%).

Characterization: ^1H NMR and FTIR spectra are consistent with that of the homopolymer prepared in methylene chloride. GPC indicates $M_n = 4.4 \times 10^3$, $M_w =$
10 1.1×10^3 , MWD = 2.58.

EXAMPLE 24

Polymerization of Styrene In Liquid Carbon Dioxide

The reaction is conducted following the same procedure described in Example 23, with the following
15 changes. No tetrabutylammonium chloride is added. The 1-chloro-1-phenyl ethane is added to the Hastelloy C-22 dish instead of the body of the cell to allow it to premix with the tin tetrachloride. Poly(styrene) (1.9903 g) is recovered. (Yield = 44%).

20 Characterization: ^1H NMR and FTIR spectra are consistent with that of the homopolymer prepared in methylene chloride. GPC indicates $M_n = 2.8 \times 10^3$, $M_w = 5.3 \times 10^3$, MWD = 1.9.

EXAMPLE 25

25 Catationic Polymerization of Isobutylene In Liquid Carbon Dioxide

Isobutylene is polymerized with an initiator system including 2-chloro-2,4,4-trimethylpentane (TMPCl)/titanium tetrachloride (TiCl_4)/Lewis bases, where
30 the Lewis base include dimethyl sulfoxide, acetamide, or ethyl acetate, in liquid and supercritical carbon dioxide using the procedure of Example 23 above. This monomer has previously been polymerized in liquid solvents, such

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as methyl chloride. See, M. Sawamoto, *Prog. Polym, Sci.* 16:111 (1991).

EXAMPLE 26

Cationic Copolymerization of Styrene and Isobutylene 5 in Carbon Dioxide

Styrene is copolymerized with isobutylene using 2-methoxy-2-propyl benzene and titanium tetrachloride in the presence of di-*t*-butyl pyridine using the method described in **Example 23** above with one change. The
10 second monomer (styrene) is added to the cell using a high pressure syringe once the isobutylene has been consumed in the reaction. It is known that these two monomers can form copolymers cationically in the mixed solvent system methyl chloride/methyl cyclohexane. See,
15 J. Kennedy, et al. *Makromol. Chem., Macromol. Symp.* 51:1269 (1991).

EXAMPLE 27

Block Copolymerization of Isobutylene and Methyl Vinyl Ether

20 Isobutylene is cationically block copolymerized with methyl vinyl ether using the $\text{TMPCl}/\text{TiCl}_4$ initiating system described in **Example 25** in the presence of tetrabutylammonium chloride in liquid and supercritical carbon dioxide using the procedure described in **Example**
25 **26**, where methyl vinyl ether is the second monomer. It is known that these monomers can form block copolymers cationically in mixed solvent systems such as methyl chloride/*n*-hexane or methylene chloride/*n*-hexane. See, J. Kennedy, et al., *Macromolecules* 25:1642 (1992).

EXAMPLE 28

Cationic Copolymerization of Isobutylene and Isoprene

30 Isobutylene is cationically block copolymerized with isoprene using cumyl acetate or boron trichloride in

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liquid and supercritical carbon dioxide using the procedure described in Example 26. Isoprene is the second monomer. It is known that these monomers can form block copolymers cationically in methyl chloride. See, 5 J. Kennedy, et al. *Macromolecules* 25:1771 (1992).

EXAMPLE 29

Cationic Polymerization of Cyclic Carbonates

Cyclic carbonates are polymerized cationically using methyl triflate, methyl iodide, or benzyl bromide 10 in liquid or supercritical carbon dioxide according to the method described in Example 17 above.

EXAMPLE 30

Cationic Polymerization of Oxetanes in Carbon Dioxide

Oxetanes are polymerized cationically using 15 strong acids or Lewis acids and preinitiators such as alcohols, ethers, and esters in liquid and supercritical carbon dioxide as described in Example 17 above.

EXAMPLE 31

Cationic Copolymerization of Oxetanes

20 and Cyclic Carbonates

Oxetanes, are copolymerized cationically with cyclic carbonates using methyl triflate or boron trifluoride diethyl etherate in liquid and supercritical carbon dioxide as described in Example 17 above, with one 25 exception. The oxetane and the cyclic carbonate are added simultaneously to the cell. The initial cell temperature is held at 0°C until the oxetane monomer is consumed. The temperature is then raised to 30°C while the cyclic carbonate monomer is consumed. It has been 30 previously known that these monomers could be copolymerized in methylene chloride and deuterated chloroform. See, T. Endo, et al., *Macromolecules* 26:7106 (1993).

EXAMPLE 32

Cationic Copolymerization of Other Cyclic Monomers

Cyclic monomers, such as oxiranes, tetrahydrofuran, trioxane, and oxazolines are polymerized
5 cationically using: (1) triflic acid or (2) Lewis acids and some proton source such as water or alcohols, in liquid and supercritical carbon dioxide as described in **Example 17** above. It has been known that these monomers could be cationically polymerized in solvents such as
10 nitromethane, methylene chloride, and carbon tetrachloride. See, E. Goethals, *Makromol. Chem., Macromol. Symp.* 42/43:51 (1991).

EXAMPLE 33

Polymerization of Formaldehyde in Carbon Dioxide

15 Formaldehyde is polymerized cationically using hydrochloric acid or Lewis acids such as boron trifluoride and water in liquid and supercritical carbon dioxide as described in **Example 17** above.

EXAMPLE 34

20 Polymerization of 3,3'-bisethoxymethyl oxetane (BEMO) In Liquid Carbon Dioxide in the Presence of Surfactant

The high pressure cell is equipped with a hastelloy C-22 dish to allow both monomer and catalyst to be added to the cell before the carbon dioxide while
25 avoiding premix. Poly(1,1 dihydroheptafluorobutoxy methyl oxetane) (p(FOX7)) (0.9902 g) is added to the cell. BEMO (4.8 mL, 4.8 g) is added to the body of the cell via syringe under an argon atmosphere. Boron trifluoride tetrahydrofuranate (BF₃-THF) (0.28 mL, 0.69
30 mmol) is added to the hastelloy dish via syringe under an argon atmosphere. The cell is equipped with a mechanical stirrer to allow the contents to be agitated during the reaction and temperature is maintained near 5°C using a circulating cold bath and a cooling coil around the cell.

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Carbon dioxide is added to the cell using an ISCO high pressure syringe pump, to achieve a pressure of 4267 psi. The reaction proceeds for six hours during which time the solution changes from clear to an opaque, "milky" dispersion. The reaction is terminated by venting the dispersion into deoxygenated, deionized water and injecting 2 mL of water into the cell. The polymer is collected and dried overnight under vacuum. Poly(BEMO) (3.1731 g) is recovered. (Yield = 66%).

Characterization: GPC indicates $M_n = 1.7 \times 10^3$ g/mol, $M_w = 5.4 \times 10^3$ g/mol, and MWD = 3.1.

EXAMPLE 35

Polymerization of 3,3'-bisethoxymethyl oxetane (BEMO) in Liquid Dioxide in the Presence of Surfactant

Reaction is set up as described in Example 34, except poly(1,1-dihydroperfluorooctyl acrylate) (p(FOA)) is used as the surfactant instead of poly(FOX7). Carbon dioxide is added to a pressure of 4200 psi. Stirring is halted after 4 hours, 25 minutes has elapsed. The "milky" dispersion described in Example 34 did not precipitate after termination of stirring. Reaction is terminated after a total reaction time of 4 hours, 35 minutes by venting into deoxygenated methanol and addition of 4 mL of deoxygenated methanol to the depressurized cell. Poly(BEMO) (3.043 g) is recovered. (Yield = 63%).

Characterization: GPC indicates $M_n = 1.4 \times 10^4$ g/mol, $M_w = 4.6 \times 10^4$ g/mol, and MWD = 3.3

EXAMPLE 36

Polymerization of Isobutylene in Liquid Carbon Dioxide in the Presence of Surfactant

p(FOA) (0.8403 g) is added to the high pressure reactor. Tin tetrachloride (0.05 mL, .43 mmoles) is added to the cell via syringe under an argon atmosphere.

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Carbon dioxide is added as described in **Example 34** to a pressure of 1285 psi. Cell temperature was 1.2°C. Isobutylene (3.4 g, 0.06 moles) is added slowly using a high pressure syringe pump to a final cell pressure of 4150 psi. The reaction began clear, but became increasingly cloudy as the reaction proceeds. Reaction proceeded for twenty-two hours at which time it is terminated by depressurization of the cell contents into deoxygenated methanol and injection of 3 mL of deoxygenated methanol into the cell. The product polymer with surfactant can be redispersed in Freon-113 as a stable suspension. Poly(isobutylene) (0.57 g) is recovered, (17% yield).

Characterization: GPC indicated a product of bimodal molecular weight, with peak molecular weights of 1.8×10^3 g/mol and 3.9×10^3 g/mol.

The foregoing is illustrative of the present invention and is not to be construed as limiting thereof. The invention is defined by the following claims, with equivalents of the claims to be included therein.

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That Which Is Claimed Is:

1. A method of carrying out the cationic polymerization of a monomer in carbon dioxide, the method comprising:
 - (a) providing a reaction mixture comprising
5 carbon dioxide, a monomer, a catalyst, and a cationic polymerization initiator, wherein said cationic polymerization initiator is capable of initiating the cationic polymerization of said monomer;
 - (b) polymerizing said monomer in said reaction
10 mixture to form a polymer.
2. The method according to Claim 1, wherein the reaction mixture comprises a heterogeneous reaction mixture.
3. The method according to Claim 1, wherein
15 the reaction mixture comprises a homogeneous reaction mixture.
4. The method according to Claim 1, wherein said monomer is selected from the group consisting of substituted or unsubstituted vinyl ether monomers, cyclic
20 ether monomers, oxazoline monomers, hydrocarbon olefin monomer, cyclic carbonate monomers, and formaldehyde.
5. The method according to Claim 1, wherein said carbon dioxide is liquid carbon dioxide.
6. The method according to Claim 1, wherein
25 said carbon dioxide is supercritical carbon dioxide.
7. The method according to Claim 1, further comprising separating said polymer from said solution following the polymerization step.

8. The method according to Claim 1, further comprising collecting said polymer from said solution following the separating step.

9. A reaction mixture useful for the cationic
5 polymerization of a monomer capable of cationic polymerization, said mixture comprising:

- (a) at least one monomer capable of cationic polymerization;
- (b) carbon dioxide;
- 10 (c) a catalyst; and
- (d) a cationic polymerization initiator capable of initiating the cationic polymerization of said polymer.

10. The reaction mixture according to Claim 9,
15 wherein said monomer is selected from the group consisting of substituted or unsubstituted vinyl ether monomers, cyclic ether monomers, oxazoline monomers, hydrocarbon olefin monomers, cyclic carbonate monomers, and formaldehyde.

20 11. The reaction mixture according to Claim 9, wherein said carbon dioxide is liquid carbon dioxide.

12. The reaction mixture according to Claim 9, wherein said carbon dioxide is supercritical carbon dioxide.

25 13. A cationic polymerization reaction mixture produced from the cationic polymerization of a monomer capable of cationic polymerization, said reaction mixture comprising:

- (a) at least one cationic polymerization
30 polymer;
- (b) carbon dioxide;
- (c) a catalyst; and

-35-

(d) a cationic polymerization initiator capable of initiating the cationic polymerization of said polymer.

14. The reaction mixture according to Claim 5 13, wherein said monomer is selected from the group consisting of substituted or unsubstituted vinyl ether monomers, cyclic ether monomers, oxazoline monomers, hydrocarbon olefin monomers, cyclic carbonate monomers, formaldehyde.

10 15. The reaction mixture according to Claim 13, wherein said carbon dioxide is liquid carbon dioxide.

16. The reaction mixture according to Claim 13, wherein said carbon dioxide is supercritical carbon dioxide.

15 17. A polymer produced by the process according to Claim 1.

18. The method according to Claim 1, wherein said polymerizing step is carried out in the presence of a surfactant.

20 19. The reaction mixture according to Claim 9 further comprising a surfactant.

20. The reaction mixture according to Claim 13 further comprising a surfactant.

A. CLASSIFICATION OF SUBJECT MATTER
 IPC 6 C08F16/12 C08F2/06

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
 IPC 6 C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GB,A,1 172 713 (SUMITOMO CHEMICAL CO. LTD.) 3 December 1969 see claim 1 see page 2, column 2, line 117 - page 2, column 2, line 130 -----	1-20

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

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- * "E" earlier document but published on or after the international filing date
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Date of the actual completion of the international search

18 October 1995

Date of mailing of the international search report

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 95/10607

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
GB-A-1172713	03-12-69	DE-A- 1745386 US-A- 3522228	09-03-72 28-07-70

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